OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0632

Task No. NR 053-720

TECHNICAL REPORT NO. 82-01

Synthesis and Stereochemistry of Some

(Silylamino)phosphinimines

by

Robert H. Neilson and Joseph S. Engenito, Jr.

Prepared for Publication

in

Organometallics

Texas Christian University
Dept. of Chemistry
Fort Worth, TX 76129

August 1, 1982

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
82-01	AD-A118005	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Synthesis and Stereochemistry of Some (Silylamino)phosphinimines	Technical Report 1981
	6. PERFORMING ORG. REPORT NUMBER TR-82-01

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
R.H. Neilson and J. S. Engenito, Jr.	N00014-79-C-0632

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Texas Christian University Fort Worth, TX 76129	NR-053-720

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research	
	13. NUMBER OF PAGES 18

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Organometallics

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Phosphinimine
Dynamic NMR
Silylamino phosphine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A series of P-alkyl-P-halo substituted (silylamino)phosphinimines $(Me_3Si)_2N-P(R)X=NSiMe_3$ are obtained either by oxidative addition of RI (R = Et, $\underline{i}$-Pr, $\underline{t}$-Bu) to $(Me_3Si)_2N-P=NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2. Reaction of the iodophosphinimines with MeLi affords the

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73

S/N 0102-LF-014-6601

20. ABSTRACT

dialkyl derivatives $(Me_3Si)_2N-P(R)Me=NSiMe_3$ (R = Et, i-Pr, t-Bu). Alcoholysis of the t-BuI product in the presence of Et_3N yields the N-H compounds $Me_3SiN(H)-P(t-Bu)OR=NSiMe_3$ (R = Me, CH_2CF_3). Variable-temperature ^1H NMR studies of these (silylamino)phosphinimines demonstrate that, depending on what substituents are present, they may be fluxional via [1,3]-silyl exchange, hindered rotation about the amino P-N bond, or [1,3]-proton exchange. The results are discussed in terms of the electronic and steric effects of the phosphorus substituents.

Accession For

NTIS GRA&I

DTIC TAB

Unannounced

Justification

By

Distribution/

Availability Codes

Avail and/or

Dist   Special

DTIC COPY INSPECTED 2

Synthesis and Stereochemistry of Some

(Silylamino)phosphinimines

ROBERT H. NEILSON* and JOSEPH S. ENGENITO, Jr.

Received _____

Abstract

- A series of P-alkyl-P-halo substituted (silylamino)phosphinimines $(Me_3Si)_2N-P(R)X=NSiMe_3$ are obtained either by oxidative addition of RI (R = Et, i-Pr, t-Bu) to $(Me_3Si)_2N-P=NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2. Reaction of the iodophosphinimines with MeLi affords the dialkyl derivatives $(Me_3Si)_2N-P(R)Me=NSiMe_3$ (R = Et, i-Pr, t-Bu). Alcoholysis of the t-BuI product in the presence of Et_3N yields the N-H compounds $Me_3SiN(H)-P(t-Bu)OR=NSiMe_3$ (R = Me, CH_2CF_3). Variable-temperature ^1H NMR studies of these (silylamino)phosphinimines demonstrate that, depending on what substituents are present, they may be fluxional via [1,3]-silyl exchange, hindered rotation about the amino P-N bond, or [1,3]-proton exchange. The results are discussed in terms of the electronic and steric effects of the phosphorus substituents.

Introduction

Several recent studies have focused on the preparative chemistry and dynamic stereochemistry of compounds containing the Si-N-P linkage. For example, their importance as polyphosphazene precursors[1,2] is now well established and their use in organophosphorus[3-5] and organometallic chemistry[6-8] is beginning to develop. Investigations of stereochemical features of these compounds, including P-N bond rotation[9,10] and silyl group rearrangements,[11-15] have also been conducted and it is these areas to which this paper is most relevant.

We report here the synthesis and dynamic NMR study of a series of (silylamino)phosphinimines of general formula:

$$\begin{array}{c} \text{Me}_3\text{Si} \\ \diagdown \\ \text{R} \diagup \end{array} \overset{\displaystyle \overset{\text{R}'}{|}}{\underset{\displaystyle \underset{\text{R}''}{|}}{\text{N-P=N-SiMe}_3}}$$
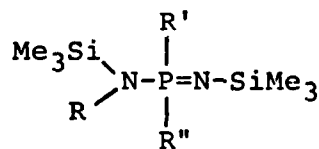
Depending on what substituents are present, it is possible to observe any of three stereochemical processes: (1) [1,3]-silyl exchange, (2) [1,3]-proton exchange if R=H, and (3) hindered rotation about the amino P-N bond.

Results and Discussion

Synthesis. Treatment of the 2-coordinate compound [bis(trimethylsilylamino)](trimethylsilylimino)phosphine (1)[16,17] with one equivalent of an alkyl iodide (except MeI) results in the rapid and quantitative formation of the 4-coordinate oxidative

addition product $\underset{\sim}{2}$ (eq 1). These phosphinimines (2) are yellow,

$$(Me_3Si)_2N-P=NSiMe_3 \quad \xrightarrow[\text{neat}]{RI} \quad (Me_3Si)_2N-\overset{\overset{R}{|}}{\underset{\underset{I}{|}}{P}}=NSiMe_3 \qquad (1)$$

$$\underset{\sim}{1}$$

$\underset{\sim}{2a}$, R = t-Bu
$\underset{\sim}{2b}$, R = i-Pr
$\underset{\sim}{2c}$, R = Et
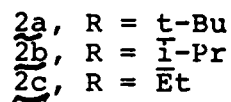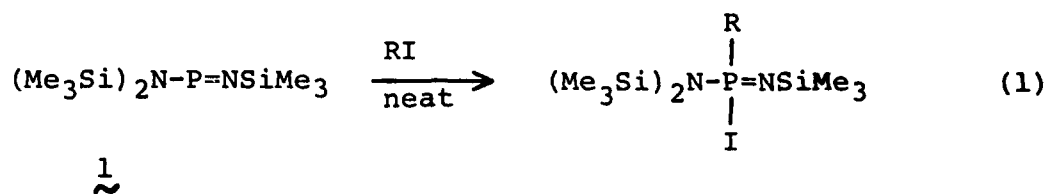
moisture-sensitive liquids of marginal thermal stability. As reported by Niecke,[18] the ethyl compound $\underset{\sim}{2c}$ can be distilled under reduced pressure without decomposition. The more sterically crowded compounds 2a and 2b, which are reported here for the first time, however, decompose rapidly on heating with elimination of Me_3SiI and formation of unidentified solid products. The characterization of these compounds, therefore, is based on NMR spectroscopy (Table I) and their derivative chemistry (see below).

Rather surprisingly, the analogous reaction with MeI is very slow and is incomplete even after stirring for 2 weeks. Analysis by NMR spectroscopy indicates the formation of a complex mixture of products. Qualitative observations indicate that the relative rate of the reaction increases markedly as the steric bulk of the alkyl group increases. This suggests that attack by the phosphine on iodine of RI with possible carbonium ion (R^+) formation may be an operative reaction pathway.

The iodomethane adduct $\underset{\sim}{2d}$ and its bromine analogue $\underset{\sim}{4}$ were prepared by the direct halogenation (eg 2) of the bis(amino)phosphine $\underset{\sim}{3}$[19]. We have previously reported a similar type of reaction

$$\underset{\underset{\sim}{3}}{(Me_3Si)_2N\overset{\overset{\displaystyle Me}{|}}{P}N(SiMe_3)_2} \xrightarrow[-Me_3SiX]{X_2} (Me_3Si)_2N\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle X}{|}}{P}}{=}NSiMe_3 \qquad (2)$$

$$\underset{\sim}{2d}, \ X = I$$

$$\underset{\sim}{4}, \ X = Br$$
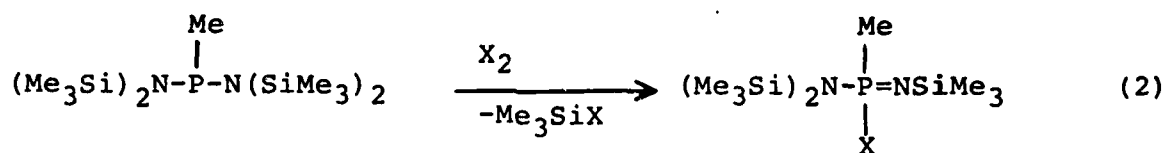
for the simple (silylamino)phosphines $(Me_3Si)_2NPR_2$.[20] Both of these P-methyl derivatives were colorless liquids that could be distilled with no evidence of decomposition, indicating that the thermal stability of such compounds is enhanced by the presence of less bulky alkyl substituents.

The P-iodophosphinimines $\underset{\sim}{2a}$-$\underset{\sim}{2c}$ were readily converted to the P-methyl derivatives $\underset{\sim}{5a}$-$\underset{\sim}{5c}$ by treatment with methyllithium in ether with activation by TMEDA (eq 3). The dimethyl analogue $(Me_3Si)_2N\text{-}PMe_2{=}NSiMe_3$ ($\underset{\sim}{5d}$), prepared by a Staudinger reaction of $(Me_3Si)_2NPMe_2$, has

$$\underset{\underset{\sim}{2}}{(Me_3Si)_2N\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle I}{|}}{P}}{=}NSiMe_3} \xrightarrow[TMEDA]{MeLi} (Me_3Si)_2N\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle Me}{|}}{P}}{=}NSiMe_3 \qquad (3)$$

$$\underset{\sim}{5a}, \ R = t\text{-Bu}$$
$$\underset{\sim}{5b}, \ R = i\text{-Pr}$$
$$\underset{\sim}{5c}, \ R = Et$$
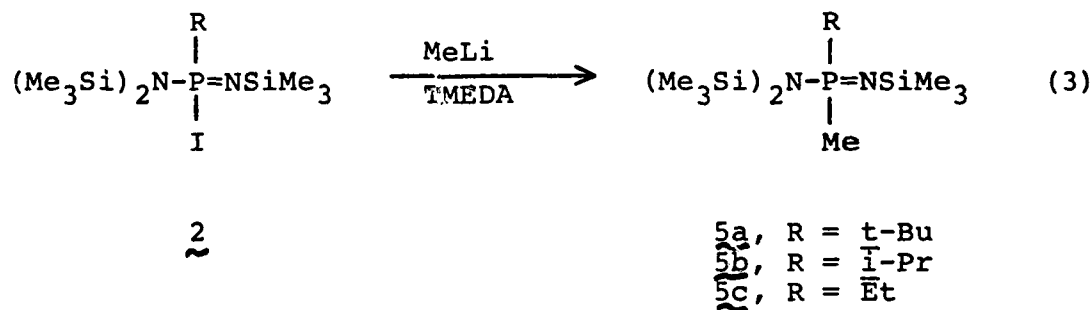
been previously reported.[21] These dialkylphosphinimines are colorless liquids which were readily purified by vacuum distillation and characterized by NMR and elemental analysis (Tables I and II).

Attempts to prepare other derivatives of the P-iodo-phosphinimines generally gave unsatisfactory results. Dehydrohalo-genation reactions of $\underset{\sim}{2}$ with amines or alcohols resulted in complex

mixtures. The N-H phosphinimines 6a and 6b were the only characterized products obtained in low yields (ca. 15%) from the reactions of 2a with alcohols (eg 4). The use of just one equivalent of the alcohol gave essentially the same results.

$$(Me_3Si)_2N\overset{\underset{\displaystyle |}{\text{t-Bu}}}{\underset{\underset{\displaystyle I}{|}}{P}}=NSiMe_3 \;+\; 2ROH \quad \xrightarrow[-2Et_3NHCl]{2Et_3N} \quad \overset{Me_3Si}{\underset{H}{>}}N\overset{\underset{\displaystyle |}{\text{t-Bu}}}{\underset{\underset{\displaystyle OR}{|}}{P}}=NSiMe_3 \qquad (4)$$

2a

6a, R = Me

6b, R = CH_2CF_3
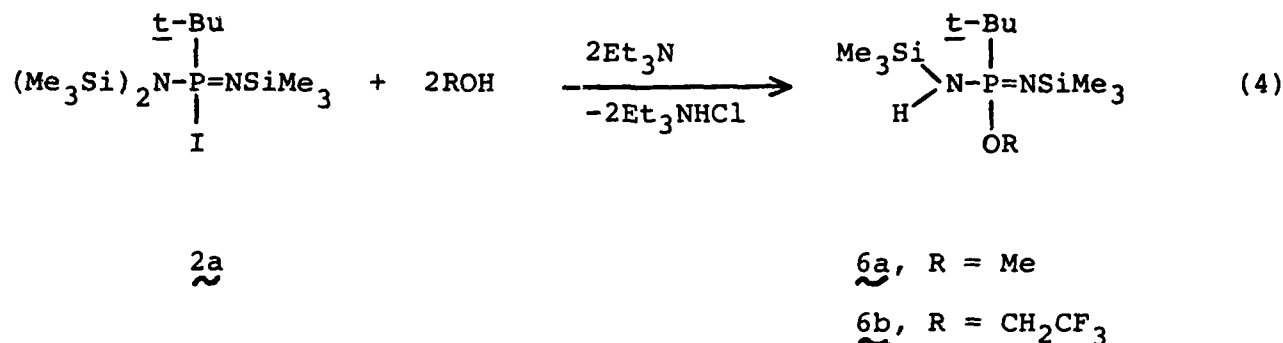
Stereochemistry. Dynamic ^{1}H NMR studies of these new (silylamino)-phosphinimines provide evidence for at least three distinct stereo-chemical processes: (1) [1,3]-silyl exchange, (2) hindered rotation about the amino P-N bond, and (3) [1,3]-proton exchange. The results obtained from these experiments are summarized in Table III.

The phenomenon of reversible [1,3] silyl exchange is common to all of the trisilylated compounds (i.e. 2a-d, 4, 5a-d). For example, the ^{1}H NMR spectrum of 2b shows the two signals (in a 2:1 intensity ratio) expected for the Me_3Si protons. At higher temperatures the [1,3]-silyl shift becomes rapid, leading to coalescence of the signals and permitting an estimate of the exchange barrier $\Delta G^{\ddagger}_{1,3}$. For 2b the process can also be monitored qualitatively by observing diastereo-topic methyl groups within the i-propyl moiety. When the [1,3]-silyl exchange is rapid, the phosphorus chirality is lost and the i-propyl

methyl groups become equivalent. The silyl exchange process is thought to be <u>intra</u>molecular since, within experimental error, the same results are obtained whether the compound is studied neat or in solution.

The $\Delta G^{\ddagger}_{1,3}$ values (Table III) all lie within the fairly narrow range of <u>ca</u>. 13.5-18.5 kcal/mole. Similar results have been reported previously for a few related compounds.[12] It is noted that the dialkylphosphinimines 5 generally have exchange barriers which are 3-4 kcal/mole lower than the corresponding alkyl(halo)phosphinimines 2 and 4. This trend is consistent with our earlier observation[12] that electron-releasing groups (e.g. Me) on phosphorus reduce the [1,3]-silyl exchange barrier. This can be rationalized as an inductive effect whereby electron-releasing substituents tend to increase the nucleophilicity of the imino nitrogen, thus facilitating its attack on the amino-SiMe$_3$ group. Moreover, alkyl groups should tend to stabilize the positive charge on phosphorus which develops in the likely transition state species.
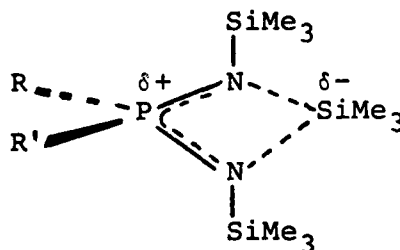
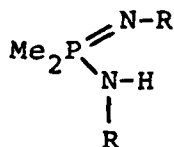The steric bulk of the substituents on phosphorus seems to have less of an affect on the $\Delta G^{\ddagger}_{1,3}$ values. For example, the results for the individual dialkyl compounds 5 differ by only <u>ca</u>. 1 kcal/mole,

suggesting that the size of the groups on phosphorus does not play a dominant role in this process. An explanation is lacking at this time, however, for the low $\Delta G^{\ddagger}_{1,3}$ value of 2a. Studies of compounds containing two bulky groups on phosphorus are needed before a more definitive conclusion about steric effects can be made.

Perhaps more significant than the [1,3]-silyl exchange is the additional observation of hindered rotation about the amino P-N bond in some of these phosphinimines. Compound 2a, for instance, exibits three distinct Me_3Si signals of equal intensity at ca. -70°C. As the temperature is raised, two of the signals broaden and coalesce at -54°C giving two peaks in a 2:1 intensity ratio. At 18°C a second coalescence point is observed, finally resulting in the single broad peak which is seen at room temperature. These results clearly show that two separate fluxional processes are operative here: (1) [1,3]-silyl exchange at higher temperatures (large $\Delta G^{\ddagger}$ value) and (2) re-stricted $P-N(SiMe_3)_2$ rotation at low temperatures (smaller $\Delta G^{\ddagger}$ value). This conclusion is also consistent with the fact that we were able to measure P-N rotation barriers only for the most sterically congested compounds (2a, 2b, and 5a). The general trend of $\Delta G^{\ddagger}_{PN}$ values in-creasing with the size of the phosphorus substituents is well docu-mented.[22]

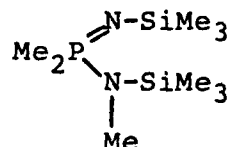Still a third type of dynamic stereochemical process appears to be occurring in the disilylated N-H compounds 6a and 6b. The Me_3Si groups in 6a, for example, appear as a single peak at room temperature but as two signals of equal intensity at temperatures below ca. -40°C. This fluxional behavior could be attributed to either [1,3]-silyl exchange as above or to [1,3]-proton exchange. Previous studies have

shown that the non-silylated phosphinimines 7 are, in fact, fluxional at room temperature[23], presumably via [1,3]-proton exchange; whereas, the disilyl(alkyl)phosphinimine 8 is not fluxional.[12] The combination of these results strongly suggests that [1,3]-proton exchange is

$$
\text{Me}_2\text{P}
\begin{array}{l}
\diagup\!\!\!= \text{N-R} \\
\diagdown \text{N-H} \\
\quad | \\
\quad \text{R}
\end{array}
\qquad\qquad
\text{Me}_2\text{P}
\begin{array}{l}
\diagup\!\!\!= \text{N-SiMe}_3 \\
\diagdown \text{N-SiMe}_3 \\
\quad | \\
\quad \text{Me}
\end{array}
$$

R = Me, t-Bu

7   8

the more likely of the two pathways for compounds 6a and 6b. Once again, it is noted that the compound with the more electron-releasing substituent (i.e. OMe in 6a) has the lower barrier to the rearrangement process.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: iodoalkanes, methanol, 2,2,2-trifluoroethanol, bromine, iodine, TMEDA, triethylamine, and methyllithium (ether solution). Benzene and ether were distilled from CaH_2 prior to use; other solvents were dried over molecular sieves. The iminophosphine $(\text{Me}_3\text{Si})_2\text{N-P=NSiMe}_3$ (1)[17] and the P,P-dimethylphosphinimine 5d[21] were prepared and purified according to published procedures. Bis[bis(trimethylsilyl)-amino](methyl)phosphine (3) was prepared by a modification of the Wilburn method;[11,24] full details of the synthesis and characterization of 3 will be reported as part of another study.[25] Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both

with ^{1}H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Micro-analytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of new compounds in this study.

P-bis(trimethylsilyl)amino-P-tert-butyl-P-iodo-N-(trimethylsilyl)-phosphinimine, 2a. The iminophosphine 1 (18.80 g, 67.5 mmol) was weighed under N_2 in a 50-mL flask which was then equipped with a magnetic stirrer and an adapter with a N_2-inlet side arm and a rubber septum. The flask was cooled to $0^{\circ}C$ and t-butyl iodide (8.04 mL, 67.5 mmol) was added via syringe. The mixture was warmed to room temperature and stirred for 2 h. Iodotrimethylsilane was removed under vacuum and identified by comparison of its ^{1}H NMR to that of an authentic sample. Nearly a quantitative yield of phosphinimine 2a remained as a viscous yellow liquid of good purity based on NMR data (Table II). Attempted distillation (bath temperature ca. $130^{\circ}C$) under vacuum resulted in decomposition with Me_3SiI evolution and formation of unidentified yellow solids. The composition of 2a was further confirmed by the preparation of its stable P-methyl derivative 5a.

The analogous compounds 2b and 2c were prepared by the same procedure except that longer reaction times (ca. 18-24 h) were required. As reported by Niecke,[18] the ethyl derivative 2c could be distilled (bp 112-115$^{\circ}C$/0.2 mm) without decomposition.

P-bis(trimethylsilyl)amino-P-iodo-P-methyl-N-(trimethylsilyl)-phosphinimine, 2d. A solution of iodine (ca. 4.6 g, 18 mmol) in benzene (60 mL) was added dropwise to a stirred solution of the bis(amino)phosphine 3[25] (6.01 g, 16.4 mmol) in benzene (30 mL) at 0°C. This titration-like addition was stopped when a faint orange color of iodine persisted in the solution. The mixture was then stirred for 90 min at room temperature before benzene and Me_3SiI were removed under vacuum. Distillation afforded 2d as a pale yellow liquid which crystallized on standing (Tables I and II). An identical procedure using bromine gave the analogous P-bromophosphinimine 4 as a colorless liquid.

P-bis(trimethylsilyl)amino-P-tert-butyl-P-methyl-N-(trimethylsilyl)-phosphinimine, 5a. Methyllithium (22.6 mL, 1.4 M in Et_2O) was added with stirring to a solution of 2a (13.95 g, 30.2 mmol; freshly prepared as described above) in Et_2O (100 mL) at 0°C. After ca. 30 min, no formation of LiCl was evident so TMEDA (4.78 mL, 31.7 mmol) was added to accelerate the reaction. The mixture was warmed to room temperature and stirred overnight. After filtration under nitrogen and solvent removal under reduced pressure, distillation afforded 5a as a colorless liquid (Tables I and II). The same procedure was used to prepare compounds 5b and 5c.

P-tert-butyl-P-methoxy-P-(trimethylsilyl)amino-N-(trimethylsilyl)-phosphinimine, 6a. A 500 mL, 3-necked flask, equipped with an addition funnel and a paddle stirrer, was charged with the iodophosphinimine 2a (13.09 g, 28.3 mmol), Et_2O (150mL), and Et_3N (7.9 mL, 56.6 mmol). The mixture was cooled to 0°C and a solution of methanol (2.3 ml, 56.6 mmol) in Et_2O (50 ml) was added dropwise. Immediate precipitation

of Et_3NHI was observed. The mixture was then warmed to room temperature and stirred overnight. Filtration under nitrogen and solvent removal under reduced pressure gave a cloudy, viscous liquid residue. Distillation gave a major fraction (ca. 5 mL, bp 65-70°C/0.2 mm) which contained 6a and other unidentified products. Redistillation afforded a pure sample of 6a as a colorless liquid (Tables I and II). Compound 6b was prepared by the same procedure from 2a and CF_3CH_2OH.

Dynamic NMR Spectra. All spectra were recorded on the Varian EM-390 instrument equipped with a standard Varian temperature controller. Temperatures were regulated to an estimated ±2°C and were calibrated against methanol and ethylene glycol reference samples. The no-exchange chemical shift difference $\Delta \nu$ and the coalescence temperature T_c were determined from the spectra. The $\Delta G^{\ddagger}$ values were calculated[26] by the so-called approximate method[27] which has been shown to give accurate results when applied to such two-site exchange processes.[28] The data are summarized in Table III. Values of $\Delta G^{\ddagger}$ measured for the same compound in different solvents never differed by more than 0.5 kcal/mole.

References and Notes

1. Wisian-Neilson, P.; Neilson, R.H. J. Am. Chem. Soc. 1980, 102, 2848.

2. Wisian-Neilson, P.; Neilson, R.H. J. Macromol. Sci. Chem. 1981, A16, 425.

3. Neilson, R.H. Inorg. Chem. 1981, 20, 1679.

4. Morton, D.W.; Neilson, R.H. Organometallics 1982, 1, 289.

5. Morton, D.W.; Neilson, R.H. Organometallics 1982, 1, 623.

6. Scherer, O.J.; Jungmann, H. Angew. Chem., Int. Ed. Engl. 1979, 18, 953.

7. Keim, W.; Appel, R.; Storeck, A.; Kruger, C.; Goddard, R. Angew. Chem., Int. Ed. Engl. 1981, 20 116.

8. Scherer, O.J.; Konrad, R.; Kruger, C.; Tsay, Yi-H. Chem. Ber. 1982, 115, 414.

9. Neilson, R.H.; Lee, R. C.-Y; Cowley, A.H. Inorg. Chem. 1977, 16, 1455.

10. Scherer, O.J.; Puttmann, M. Angew. Chem., Int. Ed. Engl. 1979, 18, 679.

11. Wilburn, J.C.; Neilson, R.H. Inorg. Chem. 1979, 18, 347.

12. Wilburn, J.C.; Wisian-Neilson, P.; Neilson, R.H. Inorg. Chem. 1979, 18, 1429.

13. Neilson, R.H.; Wisian-Neilson, P.; Wilburn, J.C. Inorg. Chem. 1980, 19, 413.

14. Glidewell, C. J. Organomet. Chem. 1976, 108, 335.

15. Hodgson, P.K.G.; Katz, R.; Zon, G. J. Organomet. Chem. 1976, 117, C63.

16. Niecke, E.; Flick, W. Angew. Chem., Int. Ed. Engl. 1973, 12, 585.

17. Scherer, O.J.; Kuhn, N. Angew. Chem., Int. Ed. Engl. 1974, 13, 811.

18. Niecke, E., Bitter, W. Chem. Ber. 1976, 109, 415.

19. See Experimental Section.

20. Wisian-Neilson, P.; Neilson, R.H. Inorg. Chem. 1980, 19, 1875.

21. Wilburn, J.C.; Neilson, R.H. Inorg. Chem. 1977, 16, 2519.

22. See reference 9 and papers cited therein.

23. Scherer, O.J.; Schnabl, G.; Lenhard, Th. Z. Anorg. Allg. Chem. 1979, 449, 167.

24. Neilson, R.H.; Wisian-Neilson, P. <u>Inorg. Chem</u>. in press.

25. Manuscript in preparation.

26. The equation $\Delta G^{\ddagger} = Tc[45.67 + 4.58 \log(Tc/\Delta\nu)]$ gives $\Delta G^{\ddagger}$ in cal/mol with Tc in ^{O}K. See Neilson, R.H.; Wells, R.L. <u>Inorg. Chem</u>. <u>1977</u>, <u>16</u>, 7.

27. Gutowsky, H.S.; Holm, C.H. <u>J. Chem. Phys</u>., <u>1956</u>, <u>25</u>, 1228.

28. Kost, D.; Carlson, E.H.; Raban, M. <u>Chem. Commun</u>. <u>1971</u>, 656.

Table I. NMR Spectroscopic Data[a]

compd	signal	1H NMR δ	1H NMR J_PH	13C NMR δ	13C NMR J_PC	31P NMR δ
(Me3Si)2N–P=NSiMe3 with t-Bu, I **2a**	Me3Si	0.35[b]		6.90	2.4	7.73
	Me3C	1.18	22.5	26.18		
	Me3C			46.35	92.2	
(Me3Si)2N–P=NSiMe3 with i-Pr, I **2b**	(Me3Si)2N	0.48		5.28	2.4	−0.81
	Me3SiN	0.12	0.4	2.72	4.9	
	PCHMe2	1.12[c]	21.0	14.88	5.5	
		1.22	27.6	17.46		
	PCHMe2	2.58	9.3	42.54	90.9	
(Me3Si)2N–P=NSiMe3 with Et, I **2c**	(Me3Si)2N	0.48		5.03	2.4	−10.72
	Me3SiN	0.12		2.01	5.5	
	PCH2Me	1.08[d]	24.3	7.41	7.9	
	PCH2Me	2.50		42.48	87.9	
(Me3Si)2N–P=NSiMe3 with Me, I **2d**	(Me3Si)2N	0.38		5.08	2.4	−27.04
	Me3SiN	0.07		1.89	5.5	
	PMe	2.30	15.0	37.79	89.7	

Table I. continued

compd	signal	^{1}H NMR δ	J_{PH}	^{13}C NMR δ	J_{PC}	^{31}P NMR δ
4 Me–(Me3Si)2N–P=NSiMe3–Br	(Me3Si)2N	0.40		5.16	2.4	2.63
	Me3SiN	0.08		2.60	4.9	
	PMe	2.12	15.6	33.75	100.1	
5a t-Bu–(Me3Si)2N–P=NSiMe3–Me	Me3Si	0.38[b]		5.93	2.5	30.15
	Me3C	1.24	15.5	26.56		
	Me3C			36.24	88.5	
	PMe	1.54	11.3	19.27	62.9	
5b i-Pr–(Me3Si)2N–P=NSiMe3–Me	Me3Si	0.26[b]		5.60	2.5	25.07
	PCHMe2	1.08[e]	17.4	16.08		
	PCHMe2	1.86	7.0	31.76	85.4	
	PMe	1.45	12.0	21.16	68.4	
5c Et–(Me3Si)2N–P=NSiMe3–Me	Me3Si	0.31[b]	.	5.32		21.10
	PCH2Me	1.16	18.0	6.22	4.9	
	PCH2Me	1.72[f]		29.36	79.4	
	PMe	1.52	12.3	23.07	72.0	

15

Table I. continued

compd	signal	^{1}H NMR		^{13}C NMR		^{31}P NMR
		δ	J_{PH}	δ	J_{PC}	δ
Me$_3$Si $\quad$ OMe $\quad$ N–P=NSiMe$_3$ $\quad$ H $\quad$ t-Bu $\qquad$ 6a	Me$_3$Si	0.10[b]		2.96		25.15
	Me$_3$C	1.04	15.9	25.58		
	Me$_3$C			33.16	127.6	
	OMe	3.42	11.6	49.22	7.3	
	NH	1.60				
Me$_3$Si $\quad$ OCH$_2$CF$_3$ $\quad$ N–P=NSiMe$_3$ $\quad$ H $\quad$ t-Bu $\qquad$ 6b	Me$_3$SiNH	0.07		2.19		24.67
	Me$_3$SiN	0.24		3.65		
	Me$_3$C	1.13	16.8	25.30		
	Me$_3$C			33.57	125.1	
	OCH$_2$	4.10[g]	7.5	59.39[h]	6.7	
	CF$_3$			124.20[h]	9.8	
	NH	1.83				

[a] Chemical Shifts downfield from Me$_4$Si for ^{1}H and ^{13}C spectra and from H$_3$PO$_4$ for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH$_2$Cl$_2$; ^{13}C and ^{31}P, CDCl$_3$. [b] Exchange-broadened singlet. [d] Complex multiplet, $J_{HH} \sim$ 7.5 Hz. [e] J_{HH} = 7.0 Hz. [f] Broad unresolved multiplet. [g] J_{FH} = 8.7 Hz. [h] J_{FCC} = 36.6 Hz; J_{FC} = 277.7 Hz.

[c] J_{HH} = 7.2 Hz. [g] J_{FH} = 8.7 Hz. [h] J_{FCC} = 36.6 Hz; J_{FC} = 277.7 Hz.

Table II.   Preparative and Analytical Data for New Phosphinimines

| compd | preparative | | analytical[a] | |
	% yield	bp, °C(mm)	% C	%H
2d	43	90-91 (0.1)[b]	28.69 (28.56)	7.26 (7.19)
4	69	68-70 (0.04)[c]	32.32 (32.16)	8.11 (8.10)
5a	54	82-84 (0.08)	47.93 (47.95)	11.09 (11.21)
5b	32	81-82 (0.04)	46.23 (46.38)	11.26 (11.08)
5c	39	64-65 (0.08)	44.69 (44.67)	11.06 (10.93)
6a	16	43-44 (0.05)	45.03 (44.86)	10.76 (10.61)
6b	14	61-62 (0.9)	39.81 (39.76)	8.43 (8.34)

[a] Calculated values in parentheses.   [b] Solid, mp 48-50°C.
[c] Solid, mp 27-32°C.

Table III. Variable-Temperature ^{1}H NMR Data[a] for (Silylamino)phos-
phinimines,

$$\underset{R}{\overset{Me_3Si}{\diagdown}}N-\underset{X}{\overset{R'}{\underset{|}{\overset{|}{P}}}}=NSiMe_3$$
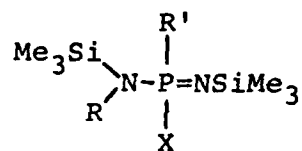
[1,3]-silyl exchange

compd	R	R'	X	solvent	Tc ($^\circ$C)	$\Delta\nu$ (Hz)	$\Delta G^\ddagger$ (kcal/mole)
2a	Me$_3$Si	t-Bu	I	CH$_2$Cl$_2$	12	33.6	14.2
2b	Me$_3$Si	i-Pr	I	neat	97	30.6	18.7
				anisole	90	26.0	18.5
2c	Me$_3$Si	Et	I	neat	60	30.6	16.8
				anisole	51	24.0	16.5
2d	Me$_3$Si	Me	I	neat	72	34.8	17.3
4	Me$_3$Si	Me	Br	neat	77	34.2	17.6
5a	Me$_3$Si	t-Bu	Me	CH$_2$Cl$_2$	18	19.8	14.8
5b	Me$_3$Si	i-Pr	Me	CH$_2$Cl$_2$	15	28.2	14.5
5c	Me$_3$Si	Et	Me	CH$_2$Cl$_2$	-3	28.8	13.5
5d	Me$_3$Si	Me	Me	CH$_2$Cl$_2$	-3	28.8	13.5

P-N(R)SiMe$_3$ rotation

compd	R	R'	X	solvent	Tc ($^\circ$C)	$\Delta\nu$ (Hz)	$\Delta G^\ddagger$ (kcal/mole)
2a	Me$_3$Si	t-Bu	I	CH$_2$Cl$_2$	-12	6.2	13.9
2b	Me$_3$Si	i-Pr	I	CH$_2$Cl$_2$	-74	5.1	10.6
5a	Me$_3$Si	t-Bu	Me	CH$_2$Cl$_2$	-54	29.1	10.8

[1,3]-proton exchange

compd	R	R'	X	solvent	Tc ($^\circ$C)	$\Delta\nu$ (Hz)	$\Delta G^\ddagger$ (kcal/mole)
6a	H	t-Bu	OMe	CH$_2$Cl$_2$	-40	16.8	11.9
6b	H	t-Bu	OCH$_2$CF$_3$	CH$_2$Cl$_2$	>45	15.3	>16.4

[a] Estimated experimental uncertainties in $\Delta G^\ddagger$ are ±0.5 kcal/mole